

THE STRUCTURES OF SOME SOLID CADMIUM DICARBOXYLATE HYDRATES

by

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INTRODUCTION

The present work is a survey of structural investigations of cadmium oxydiacetate hydrates and oxydiacetic acid. The structures will be discussed especially with regard to coordination, chelate formation and conformation of the oxydiacetate ion. The crystal structures treated in this survey have been reported in the following communications:

On the Structures of Three Different Forms of Solid Cadmium Oxydiacetate Hydrate.¹

The Structure of Cadmium Oxydiacetate - Water(2/7).²

The Structure of Monoclinic Cadmium Oxydiacetate Trihydrate.³

The Structure of Orthorhombic Cadmium Oxydiacetate Trihydrate.⁴

On the Structures of Two Crystalline Forms of Oxydiacetic Acid.⁵

When this study began in 1971, rather little was known about the coordination around cadmium. By then several investigations were in progress at this institute, concerning the complex formation of oxydiacetic, iminodiacetic and thiodiacetic acid in solution as well as in the solid state. The author therefore considered it interesting to determine the structures of the cadmium salts of these acids, the ions of which are capable of forming tridentate chelates.

Three different solid phases of cadmium oxydiacetate were obtained, and the investigation of their structures forms the major part of this work. Two phases of cadmium iminodiacetate were prepared, but as the crystals of both phases seemed to be severely affected by disorder,

they were disregarded for the time being. Only one phase of cadmium thiodiacetate has been obtained and its structure has been solved. The results are collected in an appendix⁶ to this thesis as an independent structure determination of this compound was published by Whitlow,⁷ just when the author's investigation was being finished.

Due to the considerable difference in X-ray scattering power between cadmium and the lighter atoms, the interatomic distances and angles in the organic ligands could not be determined with high accuracy. To get values for comparison in this respect, the structures of oxydiacetic acid⁵ and iminodiacetic acid⁸ were determined. The structure of thiodiacetic acid had already been solved by Paul.⁹

The coordination in cadmium salts of similar acids has also been studied by Trotter and coworkers¹⁰⁻¹⁴ and an extensive investigation of the alkali hydrogen salts of oxydi-, iminodi- and thiodiacetic acid has been made by Herbertsson.¹⁵⁻²¹

The following abbreviations will be used throughout this thesis:

CDOXY I = Cadmium oxydiacetate - water(2/7) or catena- μ -oxydiacetato - pentaquaooxydiacetatodicadmium dihydrate.

CDOXY II = Monoclinic cadmium oxydiacetate trihydrate or di- μ -oxydiacetato - bis(triaquacadmium).

CDOXY III = Orthorhombic cadmium oxydiacetate trihydrate or diaqua-cadmium oxydiacetate monohydrate.

EXPERIMENTAL

Single crystals of the three different cadmium oxydiacetate phases were prepared by slow evaporation of aqueous solutions containing equimolar amounts of cadmium nitrate and disodium oxydiacetate. The latter was made from commercial oxydiacetic acid (Merck) and sodium hydroxide. At room temperature CDOXY I and II were precipitated simultaneously and at somewhat higher temperatures, 40–50 °C, CDOXY III was the main product. The two phases of oxydiacetic acid were obtained by recrystallization of the commercial acid. The cadmium thiodiacetate monohydrate was made from cadmium nitrate, thiodiacetic acid (Fluka AG) and sodium hydroxide in the same way as the oxydiacetates.

For all substances analyses for carbon and hydrogen were made at the Division of Analytical Chemistry, University of Lund, Sweden. The cadmium content was determined by complexometric titration. The results agreed well with the calculated values and they were confirmed by the crystal structure analyses in all cases except possibly for CDOXY II, where the question of disordered water arose. The elemental analyses for CDOXY II could not settle this question as they gave values between those expected for 3 and 3.5, but somewhat closer to 3 water molecules of crystallization per formula unit.

All the structure determinations were based on three-dimensional, single-crystal X-ray data. Some information about the collection of data and the refinement is given in Table 1. A linear single-crystal diffractometer of type PAILRED was used for CDOXY III and an automatic four-circle diffractometer of type CAD-4 was used for CDOXY II and the cadmium thiodiacetate monohydrate. The photographic data for CDOXY I and the two

phases of oxydiacetic acid were collected by use of the Weissenberg equi-inclination technique with Ni-filtered $\text{CuK}\alpha$ radiation. The relative intensities of the reflexions were obtained by visual comparison with a calibrated scale. In all cases the intensities were corrected for the Lorentz and polarization effects and, with the exception of oxydiacetic acid, for absorption. Corrections for extinction were attempted for data from the CAD-4, but in both cases the extinction was found to be negligible.

Preliminary unit cell dimensions were calculated from measurements on rotation and Weissenberg photographs and more accurate values were then obtained by least-squares treatment of powder data from a Guinier-Hägg camera ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54051 \text{ \AA}$) at 22°C with aluminium (cubic, $a = 4.04934 \text{ \AA}$) as internal standard. The cell constants for cadmium thiodiacetate monohydrate were obtained by least-squares treatment of 53 θ -values measured with the CAD-4 diffractometer.

The cell parameters for the investigated compounds are listed in Table 2.

Table 1. Some data on the refinements of the crystal structures. $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$.

Compound	Method	$\mu(\text{CuK}\alpha)$ (cm^{-1})	Reflexions	Reflexions/ Parameter	R	Standard deviations in bond distances ($\times 10^3 \text{ \AA}$)
						Cd-O
CDOXY I	Film	186	1814	8.9	0.110	15 25
CDOXY II	Diffraction	205	1445	12.2	0.069	8 12
CDOXY III	Diffraction	209	558	4.7	0.054	13 22
Oxydiacetic acid	Film	13.7	396	8.2	0.081	- 5
Cadmium thiodi- acetate monohydrate	Diffraction	282	794	7.9	0.068	9 16 3*

* For Cd-S

Table 2. Crystal data.

Compound	Unit cell dimensions			Space group	V/Z ($\text{\AA}^3$)
Formula weight	($\text{\AA}$, $^\circ$, $\text{\AA}^3$)				D_x ($\text{g}\cdot\text{cm}^{-3}$)
CDOXY I	a =	7.322(1)		No. 14	496.3 (248.2)
	b =	7.301(1)	$\beta = 90.67(1)$	$P2_1/c$	2.06
	c =	37.141(4)	$V = 1985.3$	$Z = 4(8)$	
CDOXY II	a =	6.385(1)		No. 14	
	b =	10.209(1)	$\beta = 101.75(1)$	$P2_1/c$	224.1
	c =	14.047(2)	$V = 896.4$	$Z = 4$	2.21
CDOXY III	a =	7.393(1)		No. 19	219.6
	b =	8.896(1)		$P2_12_12_1$	2.26
	c =	13.354(2)	$V = 878.2$	$Z = 4$	
Oxydiacetic acid	a =	9.706(2)		No. 15	
	b =	3.941(1)	$\beta = 104.79(2)$	$C2/c$	138.9
	c =	15.027(2)	$V = 555.2$	$Z = 4$	1.60
Cadmium thiodiacetate monohydrate	a =	8.0199(6)		No. 4	176.6
	b =	5.3557(2)	$\beta = 115.960(6)$	$P2_1$	2.62
	c =	9.1480(8)	$V = 353.3$	$Z = 2$	

DETERMINATION AND REFINEMENT OF THE STRUCTURES

The structure of the monoclinic phase of oxydiacetic acid was determined by use of the symbolic addition procedure.²²⁻²³ In the other structures the positions of the cadmium atoms were obtained from three-dimensional Patterson syntheses and the remaining non-hydrogen atoms could then be located in subsequent electron difference maps. The hydrogen atoms were not found in these structures.

The atomic scattering factors, in all cases for the neutral atoms, were taken from Cromer and Waber,²⁴ International Tables for X-ray Crystallography,²⁵ Hanson et al.²⁶, and Stewart et al.²⁷. Correction for anomalous dispersion was made for CDOXY III with data from Cromer.²⁸

The computations were performed on the UNIVAC 1108 computer in Lund, Sweden. Table 3 lists the programs used.

Table 3. Computer programs used on the UNIVAC 1108 computer in Lund in the present investigation.

PIRUM: A program for indexing of powder patterns and least-squares refinement of unit cell dimensions, written by P.-E. Werner, Stockholm.²⁹

CELSIUS: A least-squares program for the refinement of unit cell dimensions written by J. Tegenfeldt, Uppsala.

PELLE: Data reduction of PAILRED data, written by G. Malmros, Lund.

PADDY: Reads CAD-4 reflexion data from magnetic tape, written by C. Svensson, Lund.

DATAP2: A program for absorption, L_p , and extinction corrections, written by Coppens, Leizerowitz and Rabinovich.³⁰ Modified in Uppsala and Stockholm.³¹

DATACC: Data processing program for four-circle diffractometer data obtained with CAD-4. Originally written by P. Coppens. Modified in Lund.

DRF: Data reduction and Fourier calculations, written by A. Zalkin, Berkeley. Modified in Uppsala and Lund.

GAASA: The program evaluates structure factor phases applying the method of symbolic addition. Written by Lindgren, Lindqvist and Nyborg.³² Modified in Lund.

LALS: Full-matrix least-squares calculations. A. Zalkin's version of UCLALS 1, originally written by Ganzel, Sparks, and Trueblood, modified in Uppsala and Lund.

PLANE: Fits a plane to a set of points by the method of least-squares,³³ written by C.-I. Brändén, Uppsala.

DISTAN: Calculation of distances and angles, written by A. Zalkin.

ORTEP: A thermal-ellipsoid plot program for crystal structure illustrations, written by C.K. Johnson.³⁴

SACTA: A program written by J. Albertsson, Lund, that prints structure factor tables.

UPALS: Full-matrix, least-squares refinement program written by J.-O. Lundgren, Uppsala. The program is based on LALS.

DESCRIPTION OF THE INVESTIGATED STRUCTURES

The structures studied in the present work are described in detail in Refs. 1-6. Only a brief survey of the main features together with a projection and stereoscopic drawings of the structures will be given here. The coordination as well as the behaviour of the organic ligands will be treated in separate chapters.

The structures of the three phases of cadmium oxydiacetate hydrate represent three different structural types. The structure of CDOXY I consists of broad, infinite zig-zag chains of composition $2\text{CdO}(\text{CH}_2\text{COO})_2 \cdot 5\text{H}_2\text{O}$, which are parallel to (102) and running in the b-direction. The chains are linked together by hydrogen bonds as seen in Fig. 1.

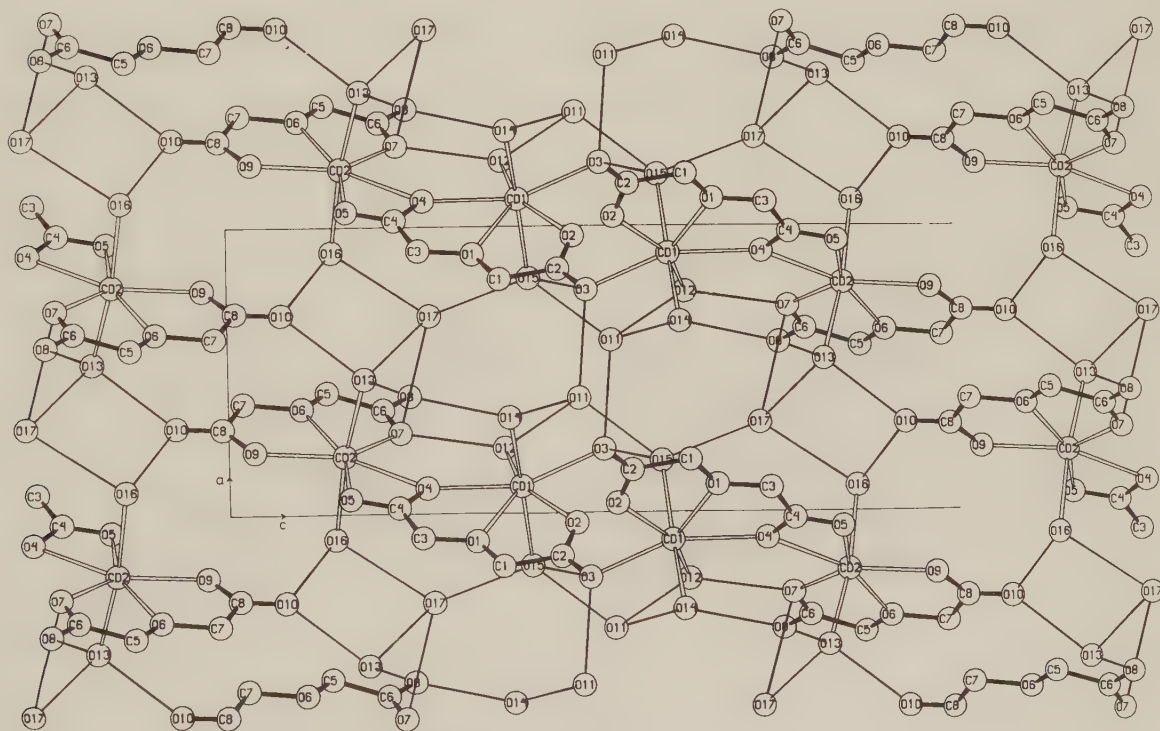


Fig. 1. A projection of part of the structure of CDOXY I along b on the ac-plane. The hydrogen bonds are marked by thin lines.

In Fig. 2 is shown how the chains in CDOXY I are built.

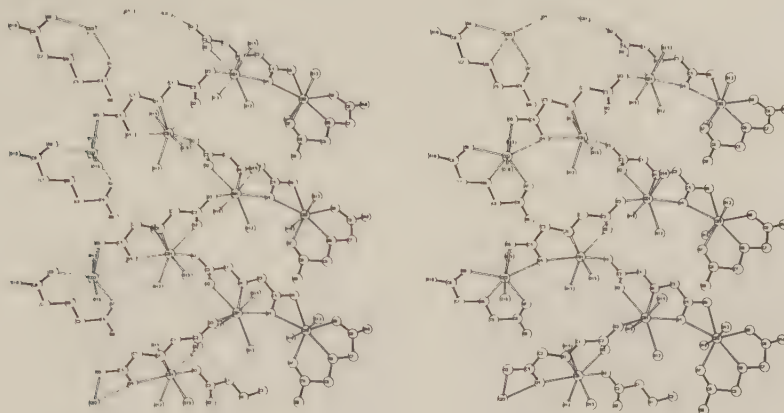


Fig. 2. A stereoscopic pair of drawings showing part of the infinite chains in CDOXY I.

The crystal structure of CDOXY II, shown in Fig. 3, is built up from discrete units of composition $2\text{CdO}(\text{CH}_2\text{COO})_2 \cdot 6\text{H}_2\text{O}$, which are held together in three dimensions by hydrogen bonds.

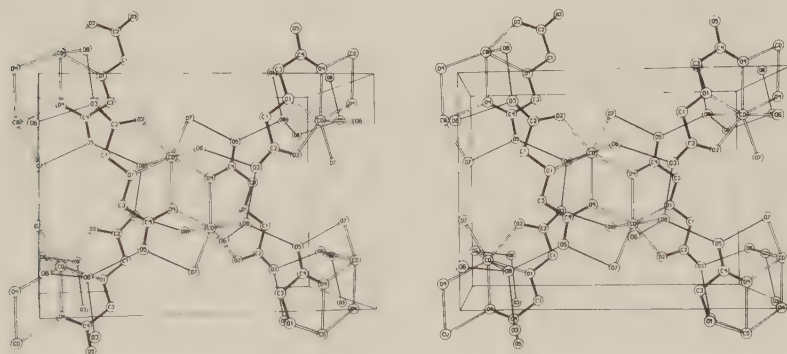


Fig. 3. Stereoscopic drawings showing the structure of CDOXY II. The hydrogen bonds are marked by thin lines. The a axis is pointing into the paper, b upwards and c to the right.

CDOXY III has a layer structure, which is shown in Fig. 4. The layers of composition $\text{CdO}(\text{CH}_2\text{COO})_2 \cdot 2\text{H}_2\text{O}$ are parallel to the ab-plane and joined in the c-direction by hydrogen bonds via the non-coordinated water oxygen o(8).

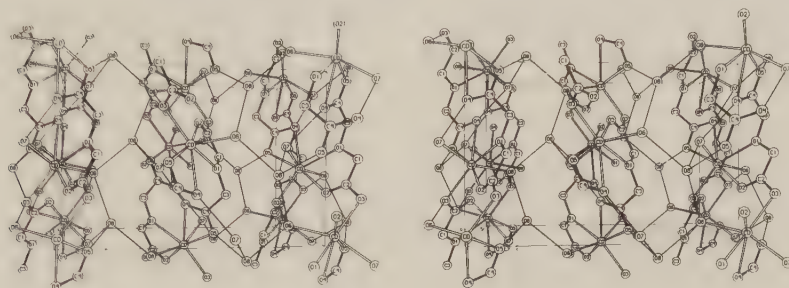


Fig. 4. A stereoscopic view of the structure of CDOXY III. The hydrogen bonds are shown by thin lines; the a axis is pointing into the paper, b upwards and c to the right.

In CDOXY I and II the non-hydrogen atoms in the oxydiacetate ion are almost coplanar whereas the anion is strongly twisted in CDOXY III, (cf. Fig. 15). The structure of cadmium thiodiacetate monohydrate, shown in Fig. 5, consists of layers of composition $\text{CdS}(\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$ which are parallel to bc and held together by relatively weak hydrogen bonds. The thiodiacetate ion is twisted about the sulphur atom (Fig. 16). This structure has also been determined by Whitlow.⁷

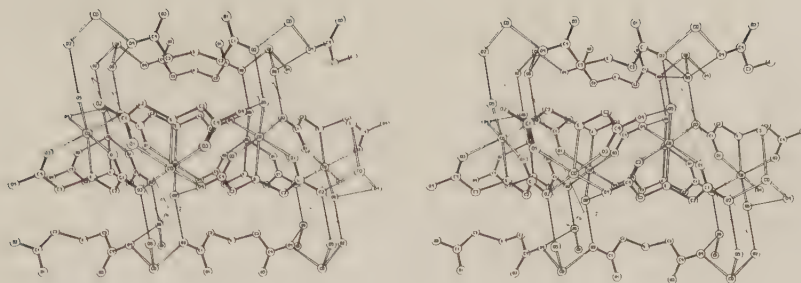


Fig. 5. A stereoscopic view of the structure of cadmium thiodiacetate monohydrate. The hydrogen bonds are marked by thin lines; a is pointing upwards, b out of the paper and c to the right.

The structure of the monoclinic phase of oxydiacetic acid is shown in Fig. 6. The strongly twisted oxydiacetic acid molecules are joined by hydrogen bonds to form infinite chains along the c-axis. The chains are held together by van der Waals forces and possibly also by hydrogen bonds. This structure was also reported by Davey and Whitlow.³⁵ In the similar thiodiacetic acid the molecules are planar according to Paul.⁹

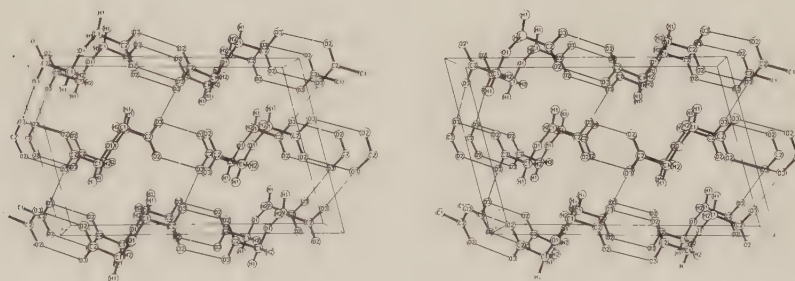


Fig. 6. A stereoscopic pair of drawings of the structure of the monoclinic phase of oxydiacetic acid. One possible hydrogen bond system is shown by thin lines. The a axis is pointing upwards, b out of the paper and c to the right.

COORDINATION AND CHELATION

As mentioned earlier, rather little was published about the coordination around cadmium when this study started. In 1972 Harrison and Trotter¹⁰ brought together what was known about Cd-O coordination. More information has been gained in the meantime especially through the investigations made by Trotter and coworkers and the main results are summarized in Table 4. A number of compounds have also been studied in which cadmium coordinates not only oxygen but also sulphur or nitrogen. Table 5 lists some of these compounds with mixed coordinations. It is seen from Table 4 that the Cd-O coordination number varies from 6 to 8, but 5 is known too from studies of some cadmium phosphates.^{36,37} When mixed coordination occurs the coordination number is 6 or 7 if N is involved, but 5 or 6 if the larger sulphur atom takes part. These results are in good agreement with those of the present investigation. In CDOXY I and II the coordination is sevenfold and the polyhedra formed are somewhat distorted pentagonal bipyramids. In CDOXY III however, the situation is more complicated. The most natural choice of coordination number is perhaps 7 with a more strongly distorted pentagonal bipyramid than in CDOXY I and II, but the coordination can also be considered as sixfold with a distorted octahedron or as eightfold with a distorted dodecahedron. In cadmium thiodiacetate monohydrate the coordination is sixfold with a distorted octahedral geometry.

The various possible geometries for sevenfold coordination are discussed by a number of authors e.g. Fergusson,³⁸ Gillespie,³⁹⁻⁴⁴ King,⁴⁵ and Muettterties and Wright.⁴⁶ King,⁴⁵ who has tabulated the geometrical possibilities with only triangular and quadrilateral faces for coordination numbers from 4 to 9, has the following to say about sevenfold coordination.

"Decisions between the various possible coordination polyhedra for seven-coordinate complexes are more difficult than for higher or lower coordination numbers for the following reasons:

- (a) more polyhedra are possible for the coordination number seven than for lower numbers;
- (b) no seven-coordinate polyhedra can be excluded as being impossible to form by $sp^m d^n$ hybridization as is the case with some of the polyhedra for coordination numbers eight and nine;
- (c) since seven is a prime number, fewer polyhedra of obviously high symmetry are found."

There are six different polyhedra of immediate interest for sevenfold coordination and four of them are shown in Fig. 7. The six polyhedra are the pentagonal bipyramid (D_{5h}), the monocapped octahedron (C_{3v}), two monocapped trigonal prisms of symmetries C_{2v} and C_{3v} , the tetragonal base-trigonal base (C_s) and the skew tetragonal base-trigonal base (C_s).



Fig. 7. Conventional perspectives of the idealised heptacoordinate models. From left to right are the C_{2v} capped trigonal prism, C_s tetragonal base-trigonal base, D_{5h} pentagonal bipyramid, and C_{3v} capped octahedron. The figure is after Muetterties and Wright. ⁴⁶

Of these, the first two have only triangular faces and in the absence of special perturbations such as nonspherical electronic configurations of the metal atom and steric constraints imposed by the ligands, they should be favoured because of the maximum number of edges and faces formed and the closeness of the approximation to the sphere.

Examples of all coordination polyhedra mentioned above except the monocapped trigonal prism C_{3v} have been found in actual structures, but the pentagonal bipyramid seems to be the most common of them. The polyhedra do not differ very much in appearance as seen from Fig. 8, which shows them in a different orientation.

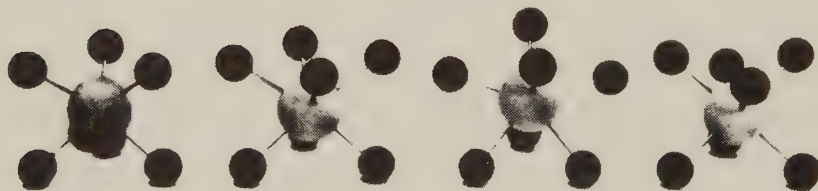


Fig. 8. Perspectives illustrating structural similarities in the idealised heptacoordinate models, which appear in the same order as in Fig. 7. This figure is also after Muetterties and Wright.⁴⁶

In many structures it is difficult to decide which of the polyhedra a given set of seven coordinating atoms comes closest as there are deviations from the ideal geometries in most cases and particularly when chelating ligands are involved in the coordination.

In CDOXY I and II the pentagonal bipyramids are rather well-defined as seen in Figs. 9 and 10.

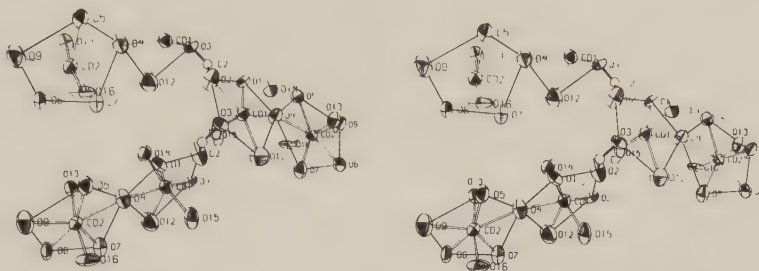


Fig. 9. The two pentagonal bipyramids in CDOXY I.

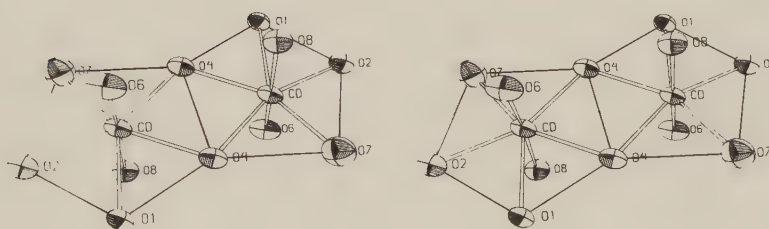


Fig. 10. The coordination in CDOXY II. Two pentagonal bipyramids have one edge in common.

There is, however, a marked distortion of the pentagonal bipyramid in CDOXY III as seen in Fig. 11. In cadmium thiodiacetate monohydrate the five oxygen atoms and the sulphur atom form an octahedron, distorted chiefly by the larger sulphur atom, Fig. 12.

As seen from Table 4 cadmium is surrounded by seven oxygen atoms in cadmium diacetate dihydrate,¹⁰ cadmium malonate monohydrate¹⁴ and cadmium nitrate dihydrate.⁴⁷ The coordination polyhedron is a distorted tetragonal base-trigonal base in the acetate and a distorted pentagonal bipyramid

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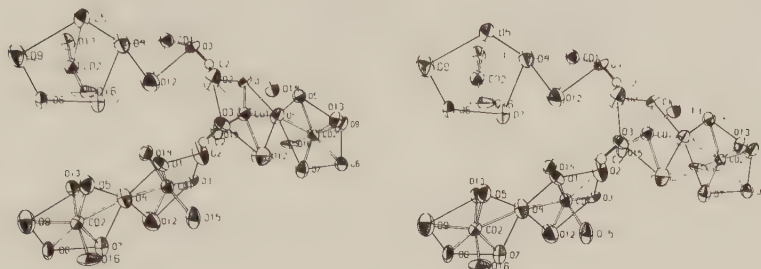


Fig. 9. The two pentagonal bipyramids in CDOXY I.

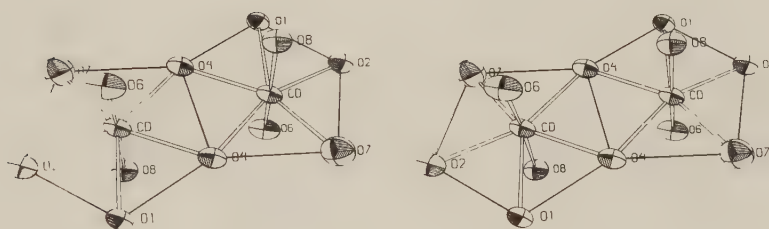


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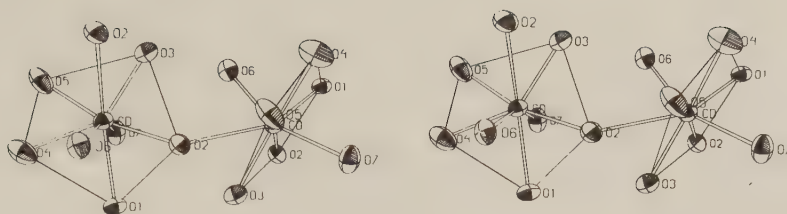


Fig. 11. The coordination around cadmium in CDOXY III. Eight oxygen atoms are shown; seven of them form a distorted pentagonal bipyramid while the eighth, O2 at the top of the left bipyramid, is further away.

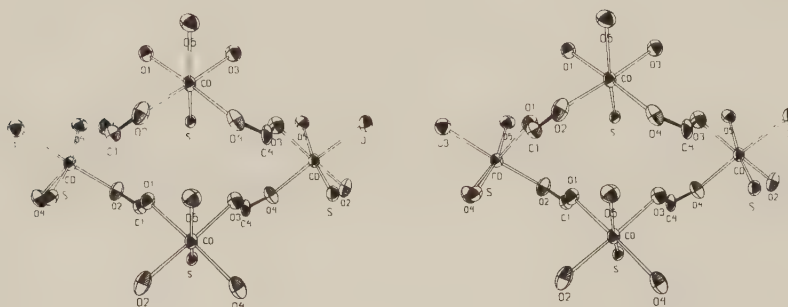


Fig. 12. The coordination in cadmium thiodiacetate monohydrate.

in the other two compounds. Among cadmium compounds with mixed coordination the dinitratotrispyridinecadmium⁴⁸ and the aquodinitratobis(quinoline)-cadmium⁴⁹ have sevenfold coordination as seen in Table 5, and in the latter compound the five oxygen atoms and the two nitrogen atoms form a distorted pentagonal bipyramid. Table 5 also gives an example of a compound in which cadmium coordinates two oxygen atoms and four sulphur atoms in an octahedral arrangement viz. the bistioureacadmium formate.⁵⁰

Table 4. Cadmium compounds in which Cd is coordinated by O only.

Compound	Formula	Coordination Number	Coordination Geometry	Range of Cd-O (Å)
Cadmium Diacetate Dihydrate ¹⁰	$\text{Cd}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$	7	Distorted tetragonal base-trigonal base	2.292-2.597(4)
Cadmium(II) Formate Dihydrate ¹¹	$\text{Cd}(\text{HCOO})_2 \cdot 2\text{H}_2\text{O}$	6	Distorted octahedron	2.243-2.326(5)
			Distorted octahedron	
Cadmium(II) Maleate Dihydrate ¹³	$\text{CdH}_2\text{C}_4\text{O}_4 \cdot 2\text{H}_2\text{O}$	6	Distorted octahedron	2.199-2.843(5)
			Distorted dodecahedron	
Cadmium(II) Malonate Monohydrate ¹⁴	$\text{CdH}_2\text{C}_3\text{O}_4 \cdot \text{H}_2\text{O}$	7	Distorted pentagonal bipyramid	2.272-2.501(7)
Catena-Di-μ-acetyl-acetonato-cadmium(II) ⁵¹	$\text{Cd}(\text{H}_7\text{C}_5\text{O}_2)_2$	6	Distorted octahedron	2.221-2.353(4)
Potassium Tris(acetylacetonato)-cadmate(II) Monohydrate ⁵²	$\text{CdK}(\text{H}_7\text{C}_5\text{O}_2)_3 \cdot \text{H}_2\text{O}$	6	Distorted trigonal prism	2.247-2.325(9)
Calcium Cadmium Acetate Hexahydrate ⁵³	$\text{CdCa}(\text{CH}_3\text{COO})_4 \cdot 6\text{H}_2\text{O}$	8	Distorted dodecahedron	2.289-2.677(8)
CDOXY I ²	$\text{CdH}_4\text{C}_4\text{O}_5 \cdot 3\frac{1}{2} \text{H}_2\text{O}$	7	Distorted pentagonal bipyramid	2.278-2.491(14)
			Distorted pentagonal bipyramid	

Table 4. cont.

Compound	Formula	Coordination Number	Coordination Geometry	Range of Cd-O (Å)
CDOXY II ³	$\text{CdH}_4\text{C}_4\text{O}_5 \cdot 3\text{H}_2\text{O}$	7	Distorted pentagonal bipyramid	2.236-2.492(8)
CDOXY III ⁴	$\text{CdH}_4\text{C}_4\text{O}_5 \cdot 3\text{H}_2\text{O}$	7 or 8	Distorted pentagonal bipyramid or distorted dodecahedron	2.269-2.841(13)
Cadmium Nitrate Tetrahydrate ⁵⁴	$\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	6 or 8	Distorted octahedron or distorted dodecahedron	2.26-2.59(2)
Cadmium Nitrate Dihydrate ⁴⁷	$\text{Cd}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$	7	Distorted pentagonal bipyramid	2.306-2.591(8)

Table 5. Cadmium compounds with mixed coordination.

Compound	Formula	Coordination Number	Coordination Geometry	Range of Cd-O and Cd-S Å
Cadmium Cyanoacetate ¹²	$\text{Cd}(\text{CH}_2\text{CNCOO})_2$	$6\left(\begin{smallmatrix} 5 & 0 \\ 1 & \text{N} \end{smallmatrix}\right)$	Distorted octahedron	2.223-2.415(4)
Dinitratotrispyridine-cadmium(II) ⁴⁸	$\text{Cd}(\text{C}_6\text{H}_5\text{N})_3(\text{NO}_3)_2$	$7\left(\begin{smallmatrix} 4 & 0 \\ 3 & \text{N} \end{smallmatrix}\right)$		2.444-2.491(10)
Aquodinitratobis(quinoline)-cadmium(II) ⁴⁹	$\text{Cd}(\text{C}_9\text{H}_7\text{N})_2(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$	$7\left(\begin{smallmatrix} 5 & 0 \\ 2 & \text{N} \end{smallmatrix}\right)$	Distorted pentagonal bipyramid	2.346-2.559(9)
Cadmium Thiogdiacetate Monohydrate ^{6,7}	$\text{CdS}(\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$	$6\left(\begin{smallmatrix} 5 & 0 \\ 1 & \text{S} \end{smallmatrix}\right)$	Distorted octahedron	$\left\{ \begin{array}{l} 2.215-2.324(9)^* \\ 2.258-2.287(6)^{**} \\ 2.635(3)^* \\ 2.663(2)^{**} \end{array} \right\}$
Cadmium(II) Bisthioglycolate ⁵⁵	$\text{Cd}(\text{SCH}_2\text{CH}_2\text{OH})_2$	$4(4 \text{ S})$	Distorted tetrahedron	2.526-2.584(1)
Bisthioureacadmium Formate ⁵⁰	$\text{Cd}[\text{SC}(\text{NH}_2)_2]_2(\text{HCOO})_2$	$5\left(\begin{smallmatrix} 1 & 0 \\ 4 & \text{S} \end{smallmatrix}\right)$	Distorted trigonal bipyramid	$\left\{ \begin{array}{l} 2.621(3) \\ 2.517-2.692(1) \end{array} \right\}$
		$6\left(\begin{smallmatrix} 2 & 0 \\ 4 & \text{S} \end{smallmatrix}\right)$	Distorted octahedron	$\left\{ \begin{array}{l} 2.28(2) \\ 2.709-2.740(9) \end{array} \right\}$

* Present work⁶

** According to Whitlow⁷

In CDOXY I, Fig. 9, the two crystallographically independent pentagonal bipyramids have one equatorial vertex in common and in CDOXY II, Fig. 10, two pentagonal bipyramids have one equatorial edge in common. The angle between the least squares planes through the oxygen atoms forming the pentagons is 20° in CDOXY I and 0° due to the symmetry in CDOXY II. The deviations from planarity in the pentagons in the cadmium oxydiacetates are given in Table 6. In CDOXY I and II there is thus oxygen bridging between cadmium atoms and the same applies to CDOXY III, Fig. 11, if the eighth oxygen atom is considered coordinated. Oxygen bridges between cadmium atoms have recently been found in a number of cadmium compounds e.g. the cyanoacetate,¹² the maleate dihydrate,¹³ the malonate monohydrate¹⁴ and the acetylacetonate.⁵¹ Infinite -O-Cd-O-Cd- spirals are found in the cadmium diacetate dihydrate.¹⁰

Table 6. Deviations (Å) from the least-squares plane through the pentagons in the cadmium oxydiacetates. In each case the plane is defined by the first five atoms. Cf. Figs. 9, 10 and 11.

CDOXY I				CDOXY II		CDOXY III	
Plane I		Plane II					
O(1)	-0.104	O(7)	0.112	O(2)	0.155	O(1)	0.033
O(2)	-0.101	O(6)	-0.126	O(1)	-0.101	O(2)	-0.034
O(3)	0.225	O(9)	0.073	O(4)	-0.009	O(3)	0.017
O(12)	-0.273	O(5)	0.007	O(4)	0.093	O(5)	0.004
O(4)	0.252	O(4)	-0.066	O(7)	-0.138	O(4)	-0.021
Cd(1)	-0.022	Cd(2)	0.037	Cd	0.004	Cd	-0.202
O(14)	2.245	O(13)	-2.269	O(6)	2.237	O(6)	-2.402
O(15)	-2.325	O(16)	2.367	O(8)	-2.306	O(7)	2.115

The coordination distances in the three cadmium oxydiacetates and in the cadmium thiodiacetate as found by the present author are collected in Table 7. For the oxydiacetates the distances from cadmium to the

Table 7. Distances in the coordination polyhedra. Cf. Figs. 9, 10, 11 and 12.

CDOXY I				CDOXY II	
Cd(1)-O(1)	2.412(14)	Cd(2)-O(7)	2.310(17)	Cd-O(2)	2.352(8)
Cd(1)-O(2)	2.433(18)	Cd(2)-O(6)	2.278(15)	Cd-O(1)	2.356(7)
Cd(1)-O(3)	2.310(12)	Cd(2)-O(9)	2.310(14)	Cd-O(4)	2.492(8)
Cd(1)-O(12)	2.338(22)	Cd(2)-O(5)	2.345(16)	Cd-O(4)	2.345(7)
Cd(1)-O(4)	2.408(13)	Cd(2)-O(4)	2.491(14)	Cd-O(7)	2.387(10)
Cd(1)-O(14)	2.280(16)	Cd(2)-O(13)	2.312(13)	Cd-O(6)	2.236(7)
Cd(1)-O(15)	2.317(16)	Cd(2)-O(16)	2.338(16)	Cd-O(8)	2.315(7)

CDOXY III		Cadmium thiodiacetate monohydrate	
Cd-O(1)	2.490(11)	Cd-O(1)	2.321(9)
Cd-O(2)	2.296(13)	Cd-O(2)	2.215(9)
Cd-O(3)	2.342(12)	Cd-O(4)	2.218(9)
Cd-O(5)	2.269(15)	Cd-O(3)	2.311(9)
Cd-O(4)	2.637(15)	Cd-O(5)	2.324(9)
Cd-O(6)	2.316(11)	Cd-S	2.635(3)
Cd-O(7)	2.341(13)		
Cd-O(2)	2.841(13)		

pentagon-forming oxygen atoms are listed first. In all cases the apices in the pentagonal bipyramids are formed by water oxygens. The Cd-O distances found in this work are seen to be in good agreement with the values for the other compounds listed in Tables 4 and 5. Bond lengths from 1.98(2) to 3.00(2) Å are given in the literature,¹⁰ but in most cases the values seem to fall in the interval 2.2 to 2.6 Å as seen in Tables 4 and 5. The coordination in cadmium thiodiacetate is shown in Fig. 12. The distances found by the author, Table 7, differ slightly from those found by Whitlow,⁷ who gives values for Cd-O from 2.258(5) to 2.287(6) Å and for Cd-S the value 2.663(2) Å, but these differences can hardly be considered significant. The Cd-S distance found is also in

good agreement with those in similar cadmium compounds with sixfold coordination of oxygen and sulphur e.g. the cadmium bithioglycolate⁵⁵ and the bithiourea cadmium formate⁵⁰ listed in Table 5. For other bond distances and angles in the coordination polyhedra the reader is referred to the separate papers.^{2,3,4,6}

In this connection some remarks will be made concerning the eighth oxygen atom in CDOXY III. As seen in Table 7 the coordination distances for the seven closest oxygen atoms in this compound range between 2.269(15) and 2.637(15) Å, which is rather normal for Cd-O bonds, even if the gap between the sixth oxygen at a distance of 2.490(11) Å and the seventh oxygen is rather large. The distance to the eighth oxygen atom, 2.841(13), is however somewhat longer than usually found in cadmium compounds of this type, and only for the cadmium maleate dihydrate¹³ Cd-O distances of this magnitude are reported. In this compound, in which Cd is octa-coordinate, two distances of 2.782(5) and 2.843(5) Å are found. The eighth oxygen atom in CDOXY III, O(2ⁱ), belongs to a carboxylate group in which the other oxygen atom, O(3ⁱ), is coordinated by the same Cd atom at a distance of 2.342(12) Å. Further O(2ⁱ) is firmly bound by another cadmium atom at a distance of 2.296(13) Å. The Cd-O(2ⁱ)-Cd bridge formed in this way is thus very unsymmetrical. Moreover the bond angle Cd-O(2ⁱ)-C(2ⁱ) is only 82.4(1.0)^o and as the distances C(2)-O(2) and C(2)-O(3), 1.241(21) and 1.266(21) Å, do not differ significantly, an angle close to 120^o should be expected. The fact that O(2ⁱ) is at a distance of 2.841(13) Å from the cadmium atom could therefore be due chiefly to a steric effect.

In the cadmium oxydiacetates the anion occurs as monodentate, bidentate and tridentate ligand; when bidentate either the ether oxygen together

with a carboxylate oxygen or the two oxygen atoms in a carboxylate group are used. The chelate bites will be discussed in the chapter on the oxydiacetate and thiodiacetate ions.

In CDOXY I (Fig. 1), Cd(1) coordinates three water molecules and two oxydiacetate ions, one tridentate and one monodentate; and Cd(2) coordinates two water molecules and two anions, one tridentate and one forming a bidentate carboxylate chelate. The oxydiacetate ion which forms the tridentate chelate with Cd(1) also forms a bidentate carboxylate chelate with the adjacent Cd(2) on one side and is bound to the adjacent Cd(1) on the other side. In this way all five coordination sites of the ligand are used for the construction of the chain Fig. 2. The other independent oxydiacetate ion in CDOXY I is coordinated only by Cd(2).

In CDOXY II, Fig. 3, there are three water molecules and two oxydiacetate ions, one tridentate and one monodentate, around cadmium, each of the two anions being coordinated by both cadmium atoms in the discrete unit. In CDOXY III, Fig. 4, cadmium is surrounded by two water molecules and three oxydiacetate ions, two of which are bidentate and one monodentate. If the coordination is considered eightfold the last one is also bidentate. This as well as one of the others is a carboxylate chelate. Each oxydiacetate ion is coordinated by three cadmium atoms.

In cadmium thiodiacetate monohydrate, Fig. 5, cadmium coordinates one water molecule and three thiodiacetate ions, one tridentate and two monodentate. The thiodiacetate ion is bound to three cadmium atoms.

THE OXYDIACETATE ION AND THE THIODIACETATE ION

The organic ligands occurring in the investigated compounds are the oxydiacetate ion and the thiodiacetate ion, the former in three cadmium salts and the latter in one. The rather heavy metal atom does not permit determinations of bond lengths and angles in the organic part with high accuracy, but the values obtained are accurate enough for discussions of the configurations in regard to planarity and chelate bites. The structure of the monoclinic phase of oxydiacetic acid⁵ was determined in order to get better values for comparison; and the studies of the alkali hydrogen salts by Herbertsson²¹ have given very accurate values for the distances and angles in both ligands. Other oxydiacetate structures that have been determined include the lanthanoid compounds,⁵⁶ the calcium oxydiacetate hydrate,⁵⁷ the copper oxydiacetate hydrate⁵⁸ and the uranyl oxydiacetate.⁵⁹ The structure of the free acid was also reported by Davey and Whitlow.³⁵

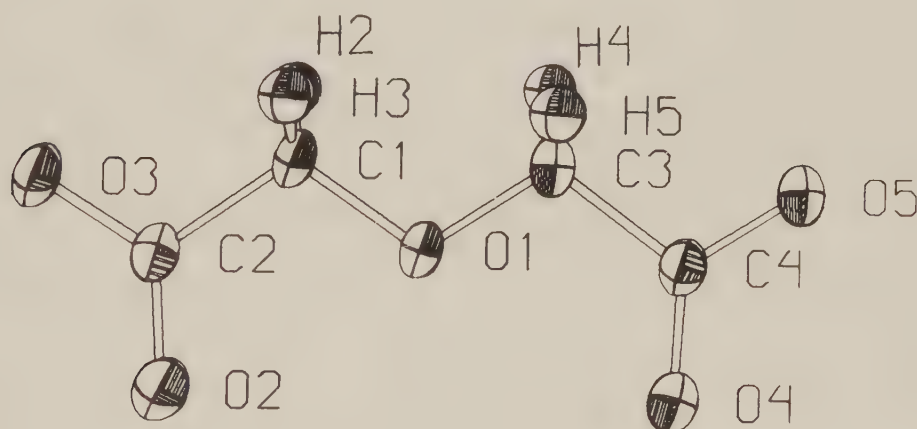


Fig. 13. The oxydiacetate ion.

The non-hydrogen atoms in the oxydiacetate ion, shown in Fig. 13, are almost coplanar in most of the investigated structures, and in all cases the $\text{O}-\text{C}-\text{C} \begin{smallmatrix} \text{O} \\ \text{O} \end{smallmatrix}$ groups have planar configurations. Deviations from

the least-squares planes through these groups are given in Table 8 for the cadmium oxydiacetates and the acid. The dihedral angles across the C(α)-C bond, defined according to Klyne and Prelog,⁶⁰ show the relative positions of the oxygen atoms in the O-C(α)-C $\begin{smallmatrix} O \\ O \end{smallmatrix}$ group and are listed in Table 9. In Tables 8, 9 and 11 the correct numbers of the atoms in Lig 2 in CDOXY I are obtained by adding 5 to the number of the oxygen atom and 4 to that of the carbon atom.

Table 8. Deviations (Å) from the least-squares planes through the independent halves in the oxydiacetate ions.

	CDOXY I		II	III	Oxydiacetic acid
	Lig 1	Lig 2			
O(1)	-0.017	-0.009	0.011	0.003	0.019
C(1)	0.037	0.010	-0.014	-0.012	-0.023
C(2)	-0.056	0.006	-0.004	0.029	-0.009
O(2)	0.029	0.002	-0.004	-0.012	-0.005
O(3)	0.008	-0.009	0.010	-0.007	0.017
O(1)	0.003	-0.021	0.038	-0.023	
C(3)	-0.003	0.027	-0.047	0.019	
C(4)	-0.002	-0.006	-0.004	0.039	
O(4)	-0.001	0.013	-0.016	-0.004	
O(5)	0.003	-0.014	0.029	-0.030	

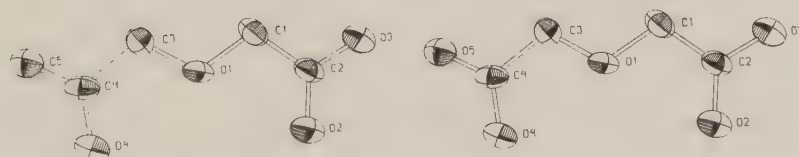


Fig. 14. The almost planar oxydiacetate ion in CDOXY II.

The oxydiacetate ion is strongly twisted about the ether oxygen in the monoclinic phase of oxydiacetic acid, in CDOXY III, and in the lithium hydrogen and copper compounds. Angles between the least-squares planes through the oxydiacetate halves in a number of compounds are given in Table 10. Fig. 14 shows the almost planar oxydiacetate ion in CDOXY II and Fig. 15 the heavily twisted ion in CDOXY III.

Table 9. Dihedral angles ($^{\circ}$) in the oxydiacetate groups.

	CDOXY I		II	III	Oxydiacetic acid
	Lig 1	Lig 2			
O(1)-C(1)-C(2)-O(2)	10.3	0.6	1.4	4.4	2.2
O(1)-C(1)-C(2)-O(3)	178.9	-178.5	-178.3	178.6	3.1
O(1)-C(3)-C(4)-O(4)	-0.2	-4.1	6.0	1.5	
O(1)-C(3)-C(4)-O(5)	179.5	177.9	174.7	174.7	

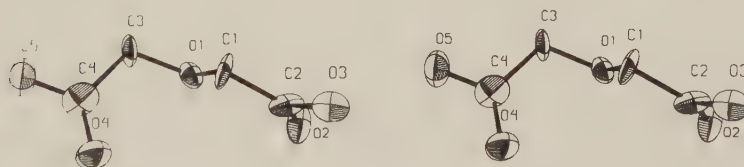


Fig. 15. The strongly twisted oxydiacetate ion in CDOXY III.

Table 10. Angles between the least-squares planes through the oxydiacetate halves.

Compound	Angle	Compound	Angle
CDOXY I	9° and 20°	LiHOXY	60°
CDOXY II	8°	NaHOXY	7.4°
CDOXY III	84°	KHOXY	5.1°
ACID	72°	RbHOXY	1°

The values for the alkali hydrogen oxydiacetates are taken from Herbertsson.²¹ It is seen that in compounds with Na^+ and larger cations the anion is almost planar. In these cases the chelate formed is tridentate. Smaller cations as Li^+ give a bidentate chelate involving the ether oxygen atom and a twisted configuration of the oxydiacetate ion. Cadmium, with ionic radius between Li^+ and Na^+ , forms two compounds with tridentate chelates and almost planar oxydiacetate ions and one with a bidentate chelate and a twisted anion, and thus seems to be on the borderline.

Table 11 lists the interatomic distances and angles in the oxydiacetate groups reported in this thesis. They are in good agreement with the corresponding values found by other authors. The most accurate set of intramolecular dimensions is given by Herbertsson.²¹

Table 11. Interatomic distances (Å) and angles ($^\circ$) in the oxydiacetate groups.

Distances	CDOXY I		II	III	Oxydiacetic acid
	Lig 1	Lig 2			
O(1)-C(1)	1.364(30)	1.451(25)	1.433(13)	1.468(22)	1.415(5)
O(1)-C(3)	1.401(20)	1.485(21)	1.380(12)	1.454(19)	
C(1)-C(2)	1.508(30)	1.491(23)	1.442(14)	1.485(24)	1.505(5)
C(3)-C(4)	1.452(28)	1.487(33)	1.508(14)	1.512(27)	
C(2)-O(2)	1.200(27)	1.234(26)	1.256(13)	1.241(21)	1.218(4)
C(2)-O(3)	1.272(25)	1.314(25)	1.289(12)	1.266(21)	1.302(4)
C(4)-O(4)	1.332(26)	1.264(28)	1.241(12)	1.219(25)	
C(4)-O(5)	1.254(20)	1.177(23)	1.246(13)	1.273(26)	
O(2)-O(3)	2.188(23)	2.275(25)	2.245(11)	2.193(18)	2.221(4)
O(4)-O(5)	2.203(19)	2.148(20)	2.210(11)	2.180(21)	
O(1)-O(2)	2.592(18)	2.584(16)	2.606(10)	2.613(18)	2.723(3)
O(1)-O(4)	2.594(21)	2.580(23)	2.609(10)	2.757(19)	
O(2)-O(4)	4.376(21)	4.292(21)	4.424(11)	4.520(20)	

Table 11. cont.

Angles	CDOXY I		II	III	Oxydiacetic acid
	Lig 1	Lig 2			
C(1)-O(1)-C(3)	112.5(1.6)	114.8(1.5)	114.1(8)	109.5(1.2)	112.2(4)
O(1)-C(1)-C(2)	112.1(2.0)	106.1(1.5)	110.0(9)	105.6(1.4)	112.3(3)
O(1)-C(3)-C(4)	107.2(1.5)	108.0(1.6)	110.8(8)	112.4(1.4)	
C(1)-C(2)-O(2)	117.6(1.9)	122.7(1.7)	121.6(8)	124.5(1.6)	123.0(3)
C(1)-C(2)-O(3)	116.7(1.9)	110.9(1.6)	114.6(9)	113.2(1.5)	113.4(3)
O(2)-C(2)-O(3)	124.6(1.7)	126.4(1.5)	123.8(9)	122.1(1.7)	123.6(3)
C(3)-C(4)-O(4)	122.6(1.5)	119.1(1.8)	119.0(9)	123.4(1.9)	
C(3)-C(4)-O(5)	120.6(1.8)	117.6(2.1)	115.7(9)	114.3(1.7)	
O(4)-C(4)-O(5)	116.8(1.8)	123.2(2.3)	125.4(9)	122.1(1.9)	

It is seen in Table 11 that the bites O(1)-O(2) and O(1)-O(4) are equal within standard deviations in all compounds except CDOXY III, where the values, 2.613(18) and 2.757(19) Å, differ significantly from each other and from the corresponding distances in the other oxydiacetates. This effect is probably caused by the different mode of coordination in CDOXY III; a bidentate chelate is formed by O(1) and O(2) while O(4) together with O(5) forms a carboxylate chelate with an adjacent cadmium atom. Significantly different bites are also found in the lithium hydrogen oxydiacetate,^{17,21} while the bites are equal in all the other alkali compounds.²¹

The thiodiacetate ion resembles the oxydiacetate ion, the only difference is that the ether oxygen has been replaced by a sulphur atom. This ion has also been studied in a number of structures, viz. the potassium, rubidium and caesium hydrogen thiodiacetates,^{18,20,21} the zinc compound,⁶¹ the neodymium complex⁶² and the free acid.⁹ The cadmium thiodiacetate was also investigated by Whitlow.⁷

In thiodiacetic acid⁹ the non-hydrogen atoms are coplanar, but in all the other studied structures the thiodiacetate ion is strongly twisted about the sulphur atom. This difference in behaviour of the oxydiacetate and the thiodiacetate ion is probably due to the difference in size of the oxygen atom and the sulphur atom. A tridentate chelate involving a large central donor atom should be formed more easily with a non-planar ligand. The non-hydrogen atoms in the ligand halves are, however, almost coplanar in all the investigated structures. The angle between the least-squares planes through the halves is 74° in cadmium thiodiacetate and 89° , 87° and 84° in the K, Rb and Cs hydrogen salts. A stereoscopic view of the thiodiacetate ion in the cadmium compound is shown in Fig. 16.

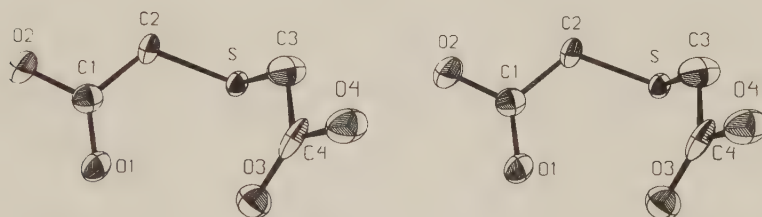


Fig. 16. The thiodiacetate ion in cadmium thiodiacetate monohydrate.

HYDROGEN BONDING

The structures reported in this thesis are held together by rather complicated hydrogen bond systems. In the cadmium compounds only water hydrogen atoms take part in the hydrogen bonds. The O-O distances are less than 3.0 Å except in two hydrogen bonds in CDOXY I where they are 3.18(2) and 3.26(3) Å; and the shortest O-O distance is 2.63(1) Å, which is found in CDOXY II. The values are thus in good agreement with those generally found in structures of this type. The hydrogen atoms involved have not been located in any of the structures and the hydrogen bond systems have accordingly been deduced from geometrical considerations. All the water hydrogen atoms except two in CDOXY III have been assigned to definite oxygen atoms and they all fit in with the structures and have approximately correct bond angles. All of them also take part in hydrogen-bonding except one belonging to O(7) in CDOXY II. This hydrogen atom must for reasons of symmetry be pointing out almost perpendicularly from the plane through the discrete unit, while O(7) has van der Waals contact (3.05(2) Å) with the centrosymmetrically related O(7) in an adjacent discrete unit.

For more details about hydrogen-bond distances the reader is referred to the various papers.²⁻⁶ The hydrogen-bond systems can be seen in Figs. 1, 3, 4, 5 and 6.

CONCLUDING REMARKS

The main purpose of this work was to study the coordination around cadmium in a number of cadmium carboxylates. It is found that coordination number 7 is preferred with oxygen in the oxydiacetates, but when a larger atom as sulphur participates in coordination the number is reduced, and found to be 6 in the thiodiacetate. The coordination polyhedron is a pentagonal bipyramid in the oxydiacetates and an octahedron in the thiodiacetate.

The configuration and chelation ability of the oxydiacetate and thiodiacetate ions have also been studied in the alkali compounds. Herbertsson²¹ found that in compounds with cations larger than Na^+ the oxydiacetate ion is planar and forms tridentate chelates, but with smaller cations, e.g. Li^+ , bidentate chelates involving the ether oxygen are formed and that the oxydiacetate ion in these cases is more or less twisted. Cadmium with ionic radius between Li^+ and Na^+ forms both tridentate and bidentate chelates with the oxydiacetate ion and thus seems to be on the borderline. When a bidentate chelate involving the ether oxygen is formed, the bite is smaller than the corresponding bite in a tridentate chelate. The oxydiacetate ion also forms a bidentate carboxylate chelate in two of the compounds. The thiodiacetate ion forms only a tridentate chelate with cadmium.

In the monoclinic phase of oxydiacetic acid the molecule is strongly twisted and thus differs from the thiodiacetic acid molecule, which is planar in the solid state. The thiodiacetate ion is, however, twisted in the cadmium compound.

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A P P E N D I X

Cadmium Thiodiacetate Monohydrate

by

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ABSTRACT

$\text{CdC}_4\text{H}_6\text{O}_5\text{S}$, F.W. 278.5 g mol^{-1} , monoclinic, space group P2_1 , $a = 8.0199(6)$, $b = 5.3557(2)$, $c = 9.1480(8) \text{ \AA}$, $\beta = 115.960(6)^\circ$, $V = 353.28 \text{ \AA}^3$ at 22°C ; $Z = 2$; $\mu(\text{CuK}\alpha) = 281.7 \text{ cm}^{-1}$; $D_m = 2.56$, $D_x = 2.618 \text{ g}\cdot\text{cm}^{-3}$. The compound has a layer structure. The layers, which are parallel to bc , are held together by relatively weak hydrogen bonds. Each Cd atom coordinates three thiodiacetate ions, one tridentate and two monodentate, and one water molecule. The coordination polyhedron is a somewhat distorted octahedron formed by five O atoms and one S atom with Cd-O distances between $2.215(9)$ and $2.324(9) \text{ \AA}$ and a Cd-S distance of $2.635(3) \text{ \AA}$. The non-hydrogen atoms are coplanar in each thiodiacetate half with an angle of 74° between the planes.

INTRODUCTION

Colourless prismatic crystals of Cd thiodiacetate monohydrate were formed at room temperature from an aqueous solution containing Na thiodiacetate and Cd nitrate in equimolar amounts. Weissenberg photographs showed the crystals to be monoclinic and the systematic absences, $0k0$ with $k = 2n$, are characteristic for $P2_1$ and $P2_1/m$. A single crystal, $0.07 \times 0.08 \times 0.05$ mm, mounted along b was used for data collection on an automatic diffractometer of type CAD-4. Intensities were recorded with $\text{CuK}\alpha$ radiation monochromatized by reflexion in a graphite crystal at a take-off angle of 5° . The ω - 2θ technique was used with scan interval $\Delta\omega = 0.80 + 0.50 \tan\theta$, the background being measured before and after each reflexion. All 799 reflexions in the interval $3.5^\circ < \theta < 37.5^\circ$ were measured, but 4 reflexions with $I < 3\sigma_c(I)$ were rejected in the subsequent calculations. A fast pre-scan was used to determine the scan-speed at which a predetermined minimum of counts (3000) was received by the detector, no reflexion, however, being measured for more than 180 s. The values of $\sigma_c(I)$ were based on counting statistics. The reflexions $\bar{2}15$, $\bar{1}15$ and $\bar{3}14$ were recorded every hour as standards. The fluctuations were random and less than 5 %. The values of I and $\sigma_c(I)$ were corrected for absorption, polarization and the Lorentz effect. The transmission factors varied from 0.038 to 0.246. Accurate lattice constants were obtained from 53 θ -values measured with the diffractometer ($\text{CuK}\alpha_1$ radiation, $\lambda = 1.54051$ Å).

The position of the Cd atom was found in a Patterson synthesis, and if the space group was chosen as $P2_1$ the remaining non-hydrogen atoms could be located in subsequent difference maps. The H atoms were not found. Full-matrix least-squares refinement minimizing $\sum w(|F_o| - |F_c|)^2$

was performed with $w = 1/(\sigma_c^2 + aF_o^2)$ where a was chosen to make the average values as equal as possible in the different $|F_o|$ and $\sin\theta$ intervals. In the last cycles of refinement anisotropic temperature factors were used for all 11 atoms making a total of 100 parameters and the value of a was 0.008. The scattering factors for Cd were those given by Cromer & Waber (1965) and for S, O and C those given by Hanson, Herman, Lea & Skillman (1964), in all cases for the neutral atoms. The final values of $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.067$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|^2]^{1/2} = 0.078$ and $S = [\Sigma w(|F_o| - |F_c|)^2 / (m-n)]^{1/2} = 0.93$. An attempt to correct for extinction showed that this effect could be neglected. In the last cycle the shifts in the parameters were less than 1 % of the estimated standard deviations. A final difference map contained residual electron densities of about $3 \text{ e } \text{\AA}^{-3}$ in the vicinity of the Cd position but was otherwise featureless. The final positional and thermal parameters are given in Tables 1 and 2. All calculations were made on the UNIVAC 1108 in Lund, Sweden (Oskarsson, 1973).

DISCUSSION

In connexion with an investigation of Cd oxydiacetates (Boman, 1974 a, b, c) the present author made a structure analysis of Cd thiodiacetate a couple of years ago in order to study the coordination about Cd, the chelates formed and the configuration of the thiodiacetate ion. But before these results were published a description of the structure appeared in a paper by Whitlow (1975). On the whole our results agree very well, but as there are minor differences on a number of points I have written a short account of my work.

The structures of K, Rb and Cs hydrogen thiodiacetates have been studied

by Herbertsson (1976 a, b), Zn thiodiacetate by Drew, Rice & Timewell (1975) and tetraaquathiodiacetatoneodymium(III) chloride by Malmberg & Oskarsson (1973). The structure of thiodiacetic acid was investigated by Paul (1967).

The structure of Cd thiodiacetate, Fig. 1, consists of infinite layers, parallel to bc, of composition $\text{CdS}(\text{CH}_2\text{COO})_2 \cdot \text{H}_2\text{O}$ which are held together by hydrogen bonds through the O(5) atoms. The construction of the layers can also be seen in Fig. 2, which shows the coordination about Cd and how the coordination polyhedra are linked together. The Cd atom coordinates five O atoms and one S atom which form an octahedron somewhat distorted mainly by the longer Cd-S distance. Three thiodiacetate ions, one tridentate and two monodentate, and one water molecule are bound by each Cd atom. In the tridentate chelate the S and one O atom from each of the two carboxy groups are used. The water O is trans to the S atom in the octahedron. From Table 3, which lists some relevant distances and angles in the coordination polyhedron, it is seen that the distances from Cd to O(1) and O(3) as well as to O(5), the water O atom, are equal within standard deviations, whereas the distances to O(2ⁱ) and O(4ⁱⁱ) also are equal but significantly shorter than the other three. In contrast to this Whitlow (1975) found four almost equal Cd-O distances, 2.276(6)-2.287(6) Å, and a significantly shorter distance to the water O atom, viz. 2.258(5) Å. Table 4 gives the deviations from the least-squares plane through four of the O atoms in the octahedron. The thiodiacetate ion is shown in Fig. 3 and some intramolecular distances and angles are listed in Table 5. The ion is heavily twisted about the S atom, but the non-hydrogen atoms in each half are almost coplanar, Table 6, with an angle of 74° between the planes. In K, Rb and Cs hydrogen thiodiacetates the corresponding angles are 89°, 87° and 84°

(Herbertsson, 1976 b). In the Zn compound (Drew et al., 1975) the anion is also twisted and has a configuration similar to that found in the present investigation. The free acid, however, is almost planar (Paul, 1967). The values of the corresponding distances and angles in the two thiodiacetate halves are almost equal which shows that the ion is almost symmetrical with a mirror plane through the S atom. All distances and angles agree well with those found in other thiodiacetates.

There is only one independent water molecule and though the H atoms were not located the hydrogen bond system could be deduced by geometrical considerations. There are two hydrogen bonds: O(5)-H...O(2) (with O(2) at $-1 + x, y, z$) which is 2.721(12) Å and O(5)-H...O(4) (with O(4) at $1 - x, y + \frac{1}{2}, 1 - z$) which is 2.911(13) Å. Of these only the first and shortest joins atoms in different layers.

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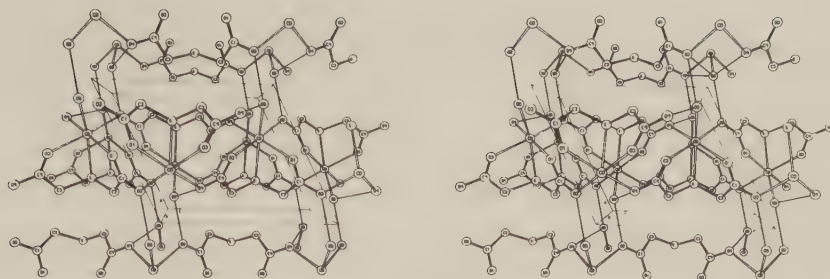


Fig. 1. A stereoscopic view of the structure of cadmium thiodiacetate monohydrate with the hydrogen bonds marked by thin lines. Figs. 1-3 were drawn by the program ORTEP.



Fig. 2. The coordination around cadmium.

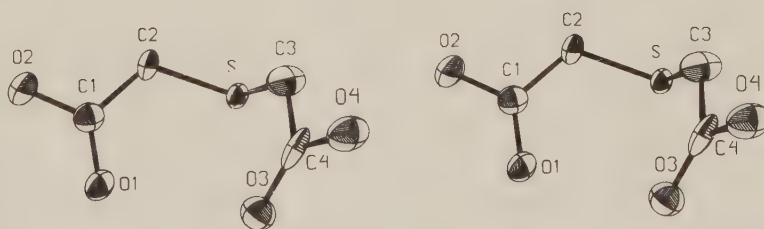


Fig. 3. The thiodiacetate ion. In Figs. 2 and 3 thermal ellipsoids were used.

Table 1. Atomic coordinates with standard deviations ($\times 10^4$) and isotropic temperature factors.

	<u>x</u>	<u>y</u>	<u>z</u>	<u>B</u> Å ²
Cd	3826(1)	2500	2010(1)	1.9
S	7158(3)	479(6)	3305(3)	1.9
O(1)	5374(12)	4915(18)	889(11)	2.6
O(2)	7767(12)	5431(20)	284(11)	3.0
O(3)	5326(13)	4864(19)	4334(10)	2.8
O(4)	7521(11)	4988(19)	6900(10)	2.9
O(5)	1472(11)	5461(18)	1141(8)	2.8
C(1)	6970(17)	4327(28)	1050(13)	2.4
C(2)	8095(16)	2224(37)	2119(14)	2.7
C(3)	8027(14)	2190(42)	5216(11)	2.9
C(4)	6821(19)	4149(29)	5458(15)	2.3

Table 2. Anisotropic thermal parameters with standard deviations ($\times 10^4$ for Cd and S and $\times 10^3$ for O and C). The form of the temperature factor is $\exp(-\beta_{11}h^2 - \dots - 2\beta_{12}hk - \dots)$. The rms components R_i ($\times 10^3$ Å) of thermal displacement along the ellipsoid axes are also listed.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}	R_1	R_2	R_3
Cd	94(2)	202(3)	74(1)	-10(2)	54(1)	-5(1)	176	127	165
S	113(4)	184(8)	77(3)	29(5)	63(3)	19(4)	191	127	152
O(1)	15(2)	26(4)	11(1)	3(2)	9(1)	2(2)	222	141	186
O(2)	14(2)	40(4)	12(1)	0(2)	9(1)	6(2)	253	141	204
O(3)	13(1)	28(3)	9(1)	2(2)	4(1)	0(2)	207	175	184
O(4)	13(1)	34(4)	10(1)	2(2)	6(1)	-5(2)	241	156	186
O(5)	14(1)	22(3)	13(1)	3(2)	8(1)	0(2)	214	158	192
C(1)	12(2)	22(4)	9(1)	0(3)	5(1)	-1(2)	185	161	178
C(2)	13(2)	44(6)	10(1)	1(4)	7(1)	9(3)	273	120	190
C(3)	11(2)	60(9)	6(1)	1(4)	2(1)	-7(3)	305	134	175
C(4)	20(2)	31(5)	11(2)	-4(3)	13(2)	-2(3)	252	97	205

Table 3. Interatomic distances (Å) and angles ($^{\circ}$) in the coordination polyhedron.

The superscripts indicate transformations applied to the coordinates given in Table 1: (i) $1-x$, $-1+(1/2+y)$, $-z$ (ii) $1-x$, $-1+(1/2+y)$, $1-z$.

Cd - O (1)	2.321 (9)	O (1) - Cd - O (2 ⁱ)	93.4 (3)
Cd - O (2 ⁱ)	2.215 (9)	O (2 ⁱ) - Cd - O (4 ⁱⁱ)	86.0 (3)
Cd - O (4 ⁱⁱ)	2.218 (9)	O (4 ⁱⁱ) - Cd - O (3)	94.5 (3)
Cd - O (3)	2.311 (9)	O (3) - Cd - O (1)	86.3 (3)
Cd - O (5)	2.324 (9)	O (5) - Cd - S	161.1 (2)
Cd - S	2.635 (3)		

O (1) - O (2 ⁱ)	3.302 (14)
O (2 ⁱ) - O (4 ⁱⁱ)	3.025 (12)
O (4 ⁱⁱ) - O (3)	3.325 (14)
O (3) - O (1)	3.169 (12)

O (5) - O (1)	3.251 (12)
O (5) - O (2 ⁱ)	3.166 (14)
O (5) - O (4 ⁱⁱ)	3.346 (13)
O (5) - O (3)	3.207 (12)

S - O (1)	3.133 (9)
S - O (2 ⁱ)	3.876 (9)
S - O (4 ⁱⁱ)	3.684 (8)
S - O (3)	3.127 (10)

Table 4. Deviations (Å) from the least-squares plane through the square of four O atoms.

Atoms defining plane: O(1), O(2ⁱ), O(4ⁱⁱ), O(3).

O(1)	-0.075
O(2 ⁱ)	0.078
O(4 ⁱⁱ)	0.074
O(3)	-0.078
Cd	-0.003
O(5)	2.319
S	-2.528

Table 5. Interatomic distances (Å) and angles (°) for the thiodiacetate ion.

S - C(2)	1.822 (14)	C(2) - S - C(3)	103.1 (0.7)
S - C(3)	1.827 (15)	S - C(2) - C(1)	118.9 (0.8)
C(2) - C(1)	1.513 (22)	S - C(3) - C(4)	119.4 (0.8)
C(3) - C(4)	1.502 (24)	C(2) - C(1) - O(1)	123.3 (1.1)
C(1) - O(1)	1.260 (15)	C(2) - C(1) - O(2)	113.5 (1.1)
C(1) - O(2)	1.281 (16)	O(1) - C(1) - O(2)	123.2 (1.2)
C(4) - O(3)	1.247 (17)	C(3) - C(4) - O(3)	122.7 (1.1)
C(4) - O(4)	1.267 (16)	C(3) - C(4) - O(4)	112.0 (1.1)
O(1) - O(2)	2.234 (13)	O(3) - C(4) - O(4)	125.3 (1.4)
O(3) - O(4)	2.233 (12)		
S - O(1)	3.133 (9)		
S - O(3)	3.127 (10)		
O(1) - O(3)	3.169 (12)		

Dihedral angles

S - C(2) - C(1) - O(1)	-2.2
S - C(2) - C(1) - O(2)	179.6
S - C(3) - C(4) - O(3)	177.5
S - C(3) - C(4) - O(4)	-2.1

Table 6. Deviations ($\text{\AA}$) from the least-squares planes through the independent halves in the thiodiacetate ion.

Atoms defining plane: (I) S, C(2), C(1), O(1), O(2); (II) S, C(3), C(4), O(3), O(4). The angle between the planes is 74° .

Atom	I	Atom	II
S	-0.006	S	-0.049
C(2)	0.011	C(3)	0.072
C(1)	-0.009	C(4)	0.002
O(1)	0.006	O(3)	0.021
O(2)	-0.002	O(4)	-0.047



